

Final Report

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From Glass-Manufacturing Waste

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Executive Summary

The objective of this 2-year research project was to develop a technology to enable the Glass Industry to recycle its glass-fiber waste. The Glass-Fiber Industry produces three solid-waste streams: glass-fiber-forming waste, fiberglass-manufacturing scrap and fiberglass-product scrap (end-of-life scrap). According to the industry document Glass: A Clear Vision for a Bright Future "... use of recycled glass lowers energy costs alone, by an average of \$4 to \$9 per metric ton compared to solely using virgin raw materials." Efforts by the industry to recycle the glass fiber forming waste resulted in an increase in the number of filament breaks occurring in the glass-fiber manufacturing process. This increased the amount of waste generated. Therefore, the glass industry needed an economical and an energy-efficient process to recycle its waste. The research resulted in the development of a process that removed contaminants and impurities from glass fiber waste and from fiberglass scrap so that the glass fibers can be recycled into value added products. In the case of the glass fiber manufacturing waste the process consists of two basic steps: (1) Washing of the waste fibers to remove excess coating solution which also contains tiny metal particles that abrade from the dies during the manufacturing process before it solidifies on the fibers, and (2) Thermal treatment of the waste fibers at temperatures below the melting point of the fibers to breakdown and oxidize the polymeric coating layer on the waste fibers. The technology was tested in the laboratory in batch and in continuous reactors and was found to be technically effective in removing the impurities and contaminants. The chemistry of the recovered glass fibers was essentially the same as the chemistry of virgin glass. Economic analysis of the process showed a potential payback of less than 2 years. In the case of the fiberglass scrap, where the only contaminant that is of concern, is the polymeric-binder, washing of the waste is not necessary. CertainTeed, one of the industrial partners, tested the process on fiberglass scrap in one of its plants in the U.S.

The approach we took in developing the technology involved identifying the contaminants followed by developing a process to remove them. After establishing the technical feasibility of the process by testing it in batch and in continuous laboratory reactors, the process was tested by one of the industrial partners in its facilities. Environmental and economic analyses of the process were then conducted to assess its environmental acceptability and economic competitiveness.

In addition to its benefits to the glass industry the research benefits the public at large by keeping this non-biodegradable waste out of the landfill. It also saves energy and reduces the amount of carbon dioxide and other pollutants associated with energy consumption.

The focus of the work was on developing a process to remove the polymeric coatings off of the glass-fibers in the waste streams. We conducted analyses on many waste samples before and after processing, and on virgin-glass samples as well, in order to identify the "foreign species" in the glass-fiber waste that are not present in the virgin glass. Analysis down to the single digit parts per billion (PPB) levels have not shown the presence of any impurities in the glass fibers themselves. The real difference was the polymeric coatings used to coat the glass fibers. We also analyzed the excess liquid that drips off of the freshly produced waste fibers. Minute amounts of metals, including noble metals, were detected in this solution. We also analyzed samples of the vitrified residue that was left at the bottom of a glass melter that was used by industry to recycle glass-fiber waste, as is. The analysis showed elevated levels of carbon and other elements in these samples. The analyses led to the following observations: (1) The polymer coating layer is a major source of contamination, (2) If the coated fibers are fed to the glass melter before the coating layer is removed it will result in the encapsulation of solid carbonaceous particulates in the molten glass, and (3) Most of the metallic particulates that erode from the dies are picked up by the solution used to coat the fibers and not in the glass fibers themselves.

To remove the metallic particulates we recommend that the glass fiber waste be washed with water while fresh before the excess coating liquid dries on the fibers. To remove the dried polymer coating layer we tested two methods: thermal treatment and chemical degradation. Both were capable of removing the coating layer. The chemical method, however, was not as effective. The thermal process, when carried out at temperatures below the melting point of the fibers, produced glass fibers from glass fiber waste with total-carbon content of less than 100 PPM, which is the level observed in the virgin "uncoated" glass.

The chemistry of the recovered glass fibers was also essentially the same as the chemistry of virgin glass. Therefore, the recovered glass fibers should be recyclable into value added products. The thermal process was also capable of removing over 99.5% of the binder material off of the fiberglass in a few minutes. This is adequate for fiberglass applications. We then developed conceptual designs for integrating the thermal treatment process with both the glass-fiber-forming and fiberglass-manufacturing processes, and performed environmental assessment and economic analysis of the processes. The economic analysis predicted a potential payback period of less than 2 years, and the process can be very environmentally friendly. Therefore, the actual accomplishments met the objective of this program.

Two inventions were disclosed by Argonne: (1) "Process to Recycle Glass Fiber Manufacturing Waste and Fiberglass Scrap." Invention Disclosure Number ANL-IN-03-129, and (2) "A process to Produce Fiberglass Panels Having Black Surfaces." Invention Disclosure Number ANL-IN-02-028. CertainTeed also had one invention disclosure. No further information is available on it at this time. A paper was also published: "A Process to Recycle Glass Fibers From Glass-Manufacturing Waste" by B. J. Jody, J. A. Pomykala Jr., E. J. Daniels, J. C. Wells, and C. E. Davis, presented at and published in the proceedings of the 2003 TMS Conference- EPD Congress, San Diego, Ca, March 3-6, 2003, pp 337-346.

A major U.S. glass fiber manufacturer has contacted Argonne National Laboratory and is "interested in perusing a partnership that ultimately helps reduce waste to landfill ...and ... will commit resources to further this project along."

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Acronyms

AES	Atomic Emission Spectroscopy
ANL	Argonne National Laboratory
DOE	Department of Energy
EDS	Electron Dispersion Spectroscopy
ICP	Inductive coupling plasma
MS	Mass Spectroscopy
PPB	Parts per Billion
PPM	Parts per Million
PPT	Parts per Trillion
SEM	Scanning Electron Microscope
TTEG	Tetraethylene glycol

Annual Report

Cover Page

Project Title: Development of a Process for the In-House Recovery and Recycling of Glass From Glass-Manufacturing Waste

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Project Objective: Develop a technology that will enable the Glass Fiber Industry to recycle its glass-fiber waste.

Background: The Glass-Fiber Industry produces three solid-waste streams: glass-fiber-forming waste, fiberglass-manufacturing scrap and fiberglass-product scrap (end-of-life scrap). The glass-fiber-forming waste is "spaghetti-like" with varying diameters and varying in lengths from a few μm to a few mm. It has a wide range of polymeric coatings or binders on the surface and contains tiny noble metal particles from the dies (bushings). Recycling of this as is resulted in an increase in the number of filament breaks occurring in the glass-manufacturing process, which increased the amount of waste generated. Therefore, recycling of this waste as is, is uneconomical and now it is landfilled. The removal of the polymeric-coating and other contaminants off of the waste glass fibers, so it can be recycled, will save the glass industry substantial amounts of energy, raw materials and money. According to the document Glass: A Clear Vision for a Bright Future "... use of recycled glass actually lowers energy costs alone, by

an average of \$4 to \$9 per metric ton compared to solely using virgin raw materials.” It is estimated that the size of this waste stream is well over 100,000 metric tons a year in the U.S. alone. Fiberglass-manufacturing scrap is generated when making final products such as fiberglass insulation batting, or fiberglass-reinforced composites such as car panels. This scrap also contains polymeric binders that are used to make “composites” with the glass. It is estimated that the size of this scrap stream is over 165,000 metric tons a year. When these products reach the end of their useful life, they constitute over 10,000,000 metric tons of waste per year.

The adopted approach in this project involved identifying the contaminants followed by developing a technology to remove them. After testing the process in the laboratory in batch and in continuous reactors, the process was tested by one of the industrial partners in its facilities. Environmental and economic analyses of the process were then conducted to assess its environmental acceptability and economic competitiveness. The same approach was applied for developing a process for removing the binder off of the fiberglass-manufacturing scrap.

Technical Discussion: The process development work is presented in two parts: Glass-Fiber-Manufacturing Waste and Fiberglass-Manufacturing Scrap.

Glass-Fiber-Manufacturing Waste

The waste generated during manufacturing of glass fibers is spaghetti-like with varying diameters (a few μm to a few mm) and lengths from a few centimeters to several meters, Figure 1. It has a polymeric coating on the surface, called sizes, which contains a number of other chemicals in small concentrations.



Figure 1. Glass-Fiber-Forming Waste

Identification of Contaminants: In order to identify contaminants in the glass fiber waste we conducted the following qualitative and quantitative analyses:

1. Scanning Electron Microscope (SEM) and Electron Dispersion Spectroscopy (EDS) analyses were conducted on glass-fiber waste samples and on “virgin” un-coated, “un-sized”, glass samples. Typical SEM pictures are shown in Figure 2. The coating material on the un-cured waste glass is very apparent, as expected. These analyses did not detect any other contaminants such as tiny metal particles. However, because we analyzed only a small number of samples, and these metallic particles could be present in concentrations on the order of parts per trillion and un-evenly distributed, we can not be certain that such particles are not present. The EDS analysis determined that Silicon, Calcium, Aluminum, Sodium and Carbon were present on the surfaces of both the glass-fiber waste and the virgin glass, Figure 3. No elements were identified on the surface of the glass-fiber waste that were not

present on the virgin glass. The carbon peak for the glass-fiber waste sample was, as expected, much larger than in the virgin sample because of the polymeric-coating material.

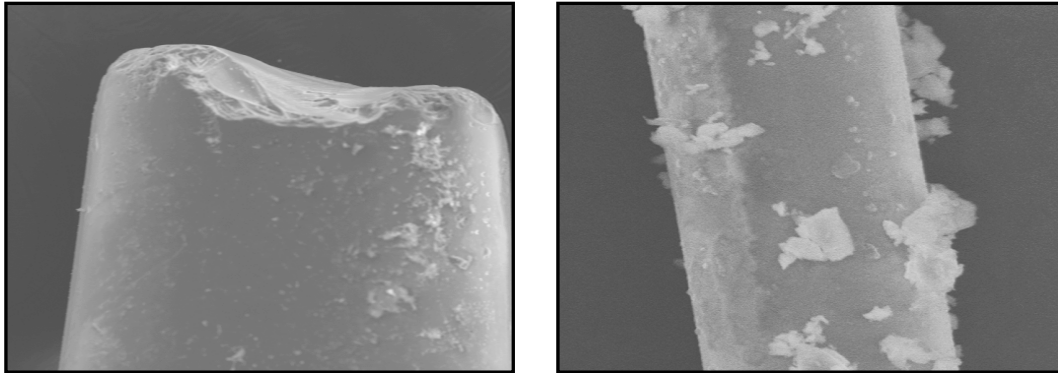


Figure 2. SEM Pictures of Virgin Glass (left) and Un-Cured, (Polymeric-Coated) Glass-Fiber-Waste (right)

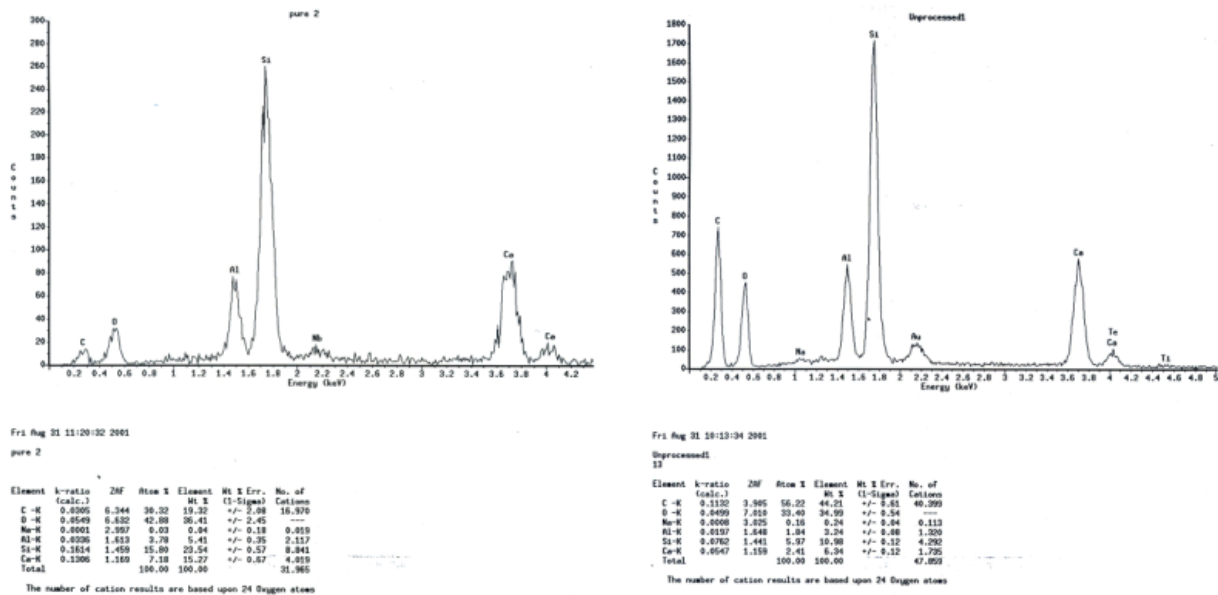


Figure 3. Same Elements Appeared in the EDS of Both Virgin (left) and Glass-Fiber-Waste (right)

- Quantitative combustible material analysis were conducted on two coated glass-fiber waste samples and on two "virgin" un-coated samples. The analytical procedure involved drying the samples at 105° C for 16 hours and then heating them in air at 650° C for 16 hours. The samples were not melted in these tests. The virgin samples contained 42 and 71 PPM of combustible material while the two glass-fiber waste samples contained 1844 and 2805 PPM of combustible material. Other waste samples treated later showed as much as 25,000 PPM of combustible materials. This clearly shows that the coating was not evenly distributed on the surface of the un-cured waste fibers.
- Total carbon content analyses were done on two "virgin" samples where the samples were first dried at 105° C for 16 hours and then heated in air at 1000° C for 16 hours. In this case,

the glass melted and so any carbon that was within the glass would have been exposed and oxidized over the prolonged exposure to oxygen at high temperature. The results showed that both samples contained less than 100 PPM of carbon and 95 PPM and 85 PPM of sulfur, respectively.

4. Inductive coupling plasma (ICP) analyses were also done on “virgin” and on glass-fiber-waste samples. The results are summarized in Table 1. No noble metals were detected. The chemistry of the waste samples and the virgin glass was essentially identical.

Table 1. Elemental Analysis of “Virgin” and Fiber-Waste Glass Samples by ICP

Element	Weight %		Element	Weight %		Element	Weight %	
	Virgin	Waste		Virgin	Waste		Virgin	Waste
Si	23.2	23.2	K	0.07	0.07	Cu	UD	UD
Ca	15.6	15.7	Zr	0.01	0.02	Ni	UD	UD
Al	6.93	6.94	Sr	0.01	0.01	Pb	UD	UD
B	2.09	1.96	Cr	0.007	0.006	Cd	UD	UD
Na	0.46	0.49	Ba	0.004	0.004	Zn	UD	UD
Ti	0.31	0.33	V	0.004	0.004	Pt	UD	UD
Fe	0.2	0.2	Mn	0.002	0.002	Pd	UD	UD
Mg	0.19	0.18	Be	UD*	UD			

* UD means undetected. The detection limits are as follows: Pt and Pd (5 PPB), Zn (3 PPB), Ni and Pb (2 PPB), Be, Cu and Cd (1 PPB).

5. ICP-MS (mass spectroscopy) analysis were done on samples that were concentrated using froth flotation techniques to help detect noble metal particles if present. About ½ pound of waste-glass fibers was crushed into a powder and processed using froth flotation to concentrate any noble metal contaminants that may be present and the concentrates were then analyzed, the results indicated that the sample contained about 3.5 PPB of platinum and about 190 PPT of iridium. Recognizing that the sample may not be a representative sample we do not consider the data to be quantitatively representative. It did, however, prove that these metals do exist in the waste glass fibers stream, most probably at the few PPT levels.
6. ICP-MS and ICP-AES (atomic emission spectroscopy) analyses were conducted on samples of fused residue that remained at the bottom of an industrial glass furnace that melted coated glass manufacturing waste. The carbon content of the two samples was 160 PPM and 180 PPM by weight, respectively. This proves that not all the coating layer was burned off during the melting process. Some thermal decomposition of the polymeric coating appears to have occurred and the resulting carbonaceous products migrated downward through the molten glass. This indicates that some tiny solid carbonaceous material is carried with the flowing molten glass and this could increase the filament breakage rate. The residue samples also showed a significant increase in the concentration of Zr, Sr, Cr, Cu, Mg, Fe, V, Ba, Mn and Zn over that in virgin glass as shown in Table 2. We are not sure why is this happening nor if this phenomenon is contributing to the increase in the frequency of filament breakage.

Table 2. Weight % of Elements in the Fused Residue

Element	Virgin Glass	Waste Fibers	Residue Samples	
			1	2
Zr	0.01	0.02	0.03	1.76
Sr	0.01	0.01	0.11	0.10
Cr	0.007	0.006	0.0157	0.0796
Cu	UD	UD	0.0020	0.0161
Mg	0.19	0.18	0.34	0.32
Fe	0.2	0.2	0.23	0.29

7. ICP-AES analysis of two samples of the excess liquid that drains off the glass fiber waste when it is produced. The first sample was collected from fresh waste and was supplied in a closed jar. The second sample was collected from the bottom of a 55-gallon drum in which glass fiber waste was shipped. At the time the second liquid sample was collected the material was sitting in the 55-gallon drum for about 2 weeks. The results are given in Table 3. The estimated platinum concentrations in these samples are 38 PPB and 44 PPB for the Jar and drum, respectively. These results indicate that the platinum concentration in the liquid is about an order of magnitude higher than in and on the glass fiber waste material itself. Once again, these results are preliminary and derived from the few samples and therefore, should be treated with care and the reported quantities may not be representative. However, it definitely suggests that washing of the glass fiber waste with fresh water should be done before treatment to remove the coating layer.

Table 3. Results of the ICP-AES Analysis of the Excess Liquid Samples

Sample ID	Sample Mass, g	Platinum mass, μ g	Iridium mass, μ g	Palladium mass, μ g
Jar Sample	~800	30.3+/-3.1	0.07+/-0.02	0.15*
Drum sample	~1000	44.2+/-4.5	< 0.02	0.32*

* The analyses for palladium were not consistent suggesting a possible interference on this element.

The results from the many analyses we did lead to the following observations and conclusions:

- The polymer coating layer constitutes the major contaminant and it should be removed before the glass is introduced into the melting furnace
- Tiny noble metal particulates are present as a contaminant most probably at the parts per trillion (PPT) range. However, it appears that most of it is present in the excess liquid solution that is used to coat the fibers. Therefore washing the fibers before the solution is allowed to dry on the fibers will reduce the problem of filament breakage.
- The chemical composition of the waste fibers is identical to that of the virgin fibers with the exception of the polymer coating layer.

Process development-Removal of Noble Metal and Other Metallic Particulates

These particulates can be present in the glass fiber, in the coating layer on the glass fibers or in the excess liquid containing the coating polymer solution which may solidify on the glass fibers. These particulates can be picked up from the “bushings” and will be essentially noble metal particulates. Other particulates could also be introduced during the handling and grinding of the glass fibers. The results of the analysis reported above indicate that a substantial portion of the noble metal particulates are in the liquid containing the coating polymer solution. Therefore, washing the fibers before the coating polymer solution solidifies on the fibers should be effective in removing these particulates. The particulates that are trapped in the coating layer will also be liberated when the coating layer is removed. For example, when the coating layer is burned off the particulates will no longer be bonded to the fibers and could be removed by washing. Particulates that are trapped in the fiber structure itself will be virtually impossible to remove without extensive and costly treatment of the glass while it is in the molten state. The particulates that are introduced during the handling and grinding of the glass fibers will not be bonded to the fibers and thus could be washed off of the glass. Therefore, in order to remove these particulates the fibers should be washed as shown in Figures 4 and 5. The fibers can also be washed only once after treatment. This has the advantage of removing particulates that were originally trapped in the coating layer but it will also result in an increase in energy consumption because energy will be used to evaporate the water that will be on the fibers after washing. In both cases grinding should be done before washing in order to wash off any particulates from the shredding and conveying equipment.

Process development-Removal of the Polymeric Coating Layer

Two methods (Thermal Treatment and Chemical Degradation) to remove the polymeric coating layer off of the glass fibers were investigated. Thermal treatment involves exposing the glass to elevated temperatures in the presence of air to burn off the polymeric coating on the glass surface. Chemical treatment involves contacting the glass fibers with chemical solutions at various temperatures to dissolve or degrade the polymeric coating. The results are discussed below.

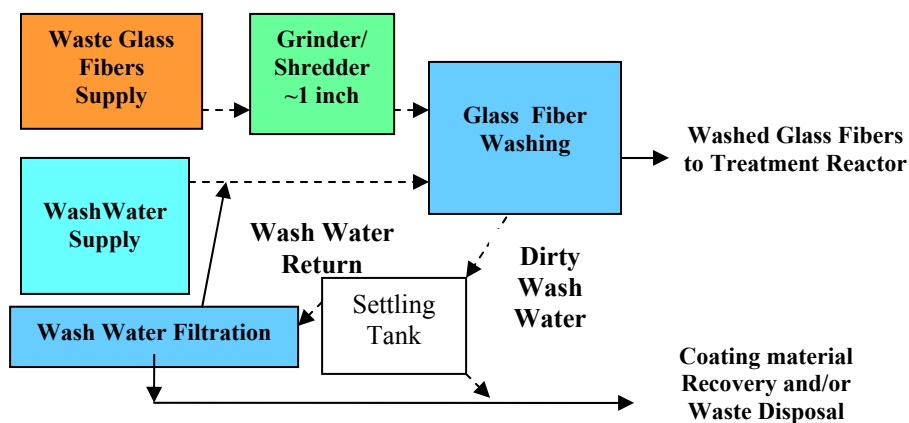


Figure 4. Conceptual Design of the Glass Fibers Shredding and Washing Operation

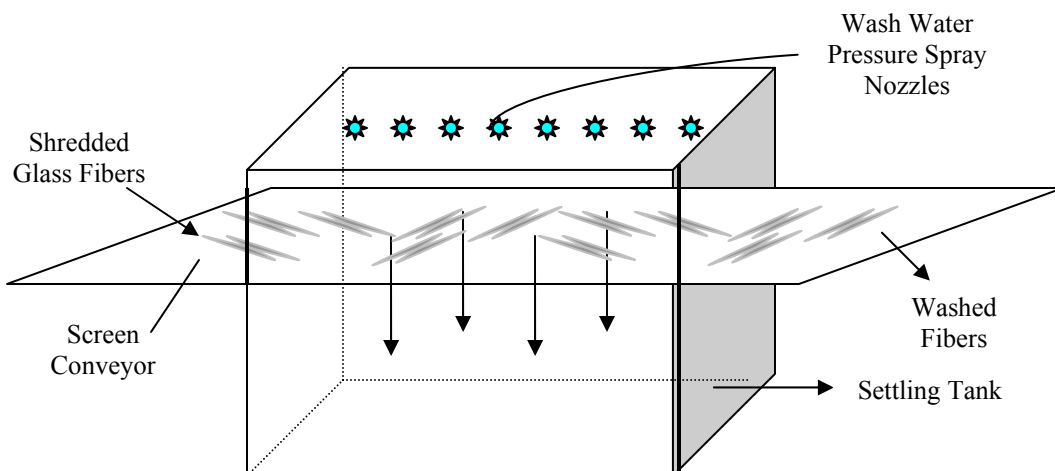


Figure 5. Conceptual Design of the Washing Operation

Thermal Treatment of the Coated Glass Fibers

We tested and evaluated the thermal treatment process to establish the technical feasibility of the process, and we conducted process-improvement studies to identify the optimum operating conditions, and to explore various potential design concepts. We also designed a gas/vapor collection subsystem for collecting samples of the evolving gases due to the break up of the polymeric-coating material, in order to identify appropriate environmental controls. We also conducted an economic evaluation of the process. Experiments were conducted in batch and continuous reactors. The results are summarized below:

- I. Processing at temperatures above the melting point of the glass resulted in the trapping of some carbonaceous material in the molten glass as shown in Figure 6. Tiny air bubbles were also trapped in the molten glass. Therefore, treatment should be done at temperatures below the melting point of the glass fibers. Hot spots in the treatment chambers should be avoided.

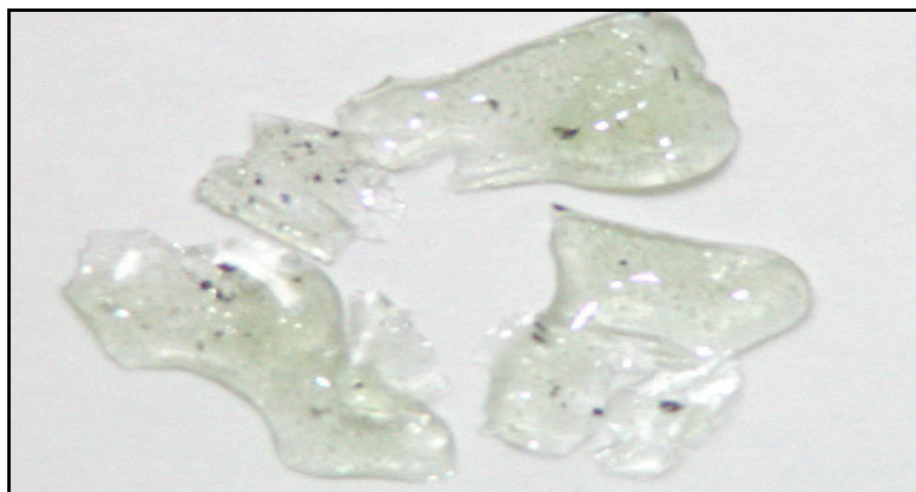


Figure 6. Glass-Fiber-Waste Treated at Temperatures Above the Glass Melting Point. The Treatment Resulted in Trapping Carbon Particles and Air Bubbles.

- II. The treated samples were analyzed to determine their residual combustible content. The results are presented in Table 4. The results show that the treated glass-fiber waste's residual combustible content is about the same as that of the virgin glass. We also conducted total-carbon analysis on the glass-fiber waste sample that was treated at 675°C for 15 minutes, which showed zero residual combustible material. The total carbon analysis results showed that it contained less than 100 PPM. ICP analysis of these treated samples showed that they have the same chemistry as the virgin glass. These results, therefore, prove that the thermal treatment process is capable of removing the polymeric coating off of the glass-fiber waste's surface.

Table 4. Residual Combustible Material on Thermally-Treated Samples
(Samples packed ~6 mm thick)

Sample Description*	Combustible Residual, PPM
Virgin Un-coated glass (Two samples)	42, 71**
Thermally Treated at 400°C for 60 minutes	0
Thermally Treated at 540°C for 10 minutes	67
Thermally Treated at 540°C for 70 minutes	70
Thermally Treated at 675°C for 15 minutes	0
** Included for comparison	

In order to determine the effect of the packing density on the process performance, which is important for scale-up considerations, dried samples of known mass were packed in open-top ceramic containers at different packing thicknesses, and placed in a preheated oven for a specified period of time. Typical results are shown in Tables 4 and 5. These results show that increasing the packing density has reduced the effectiveness of the thermal treatment process. This could be, at least partially due to the evolving gases not being able to leave the inner layers of the sample before they start to thermally decompose, leaving behind some finely dispersed solid carbonaceous particles. Slow heat transfer rates into the inner layers of the glass samples may have also contributed to this.

Table 5. Residual Combustible Material on Thermally-Treated Samples
(Samples packed ~2.5cm thick)

Sample Description	Combustible Residual, PPM
Thermally Treated at 675°C for 5 minutes	324
Thermally Treated at 675°C for 15 minutes	450
Thermally Treated at 785°C for 5 minutes	490
Thermally Treated at 785°C for 15 minutes	193
Thermally Treated at 785°C for 5 minutes	437

- III. Before a large-scale test can be conducted, the gases and vapors that evolve during the thermal treatment process have to be identified, so that the necessary environmental controls can be determined. Therefore, we designed a gas-sampling subsystem, shown schematically in Figure 7. It was fitted to the thermal treatment reactor to collect the gases and vapors that evolved so that we could have them analyzed. In order to identify some of the intermediates that may escape oxidation in tiny amounts in the field, we conducted the tests under reduced air-flow conditions to the thermal reactor. Obviously, the evolved gases depend on the types of materials present in the polymer coating layer. The composition of the total samples of emitted species is presented in Table 6.

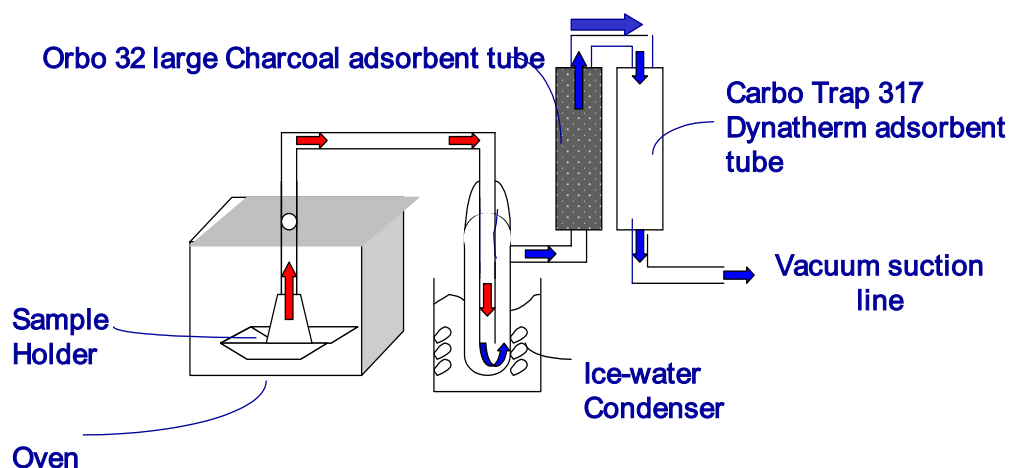


Figure 7. Gas-Sampling Subsystem.

Table 6. Emitted Pollutants in an Oxygen Deficient Environment From Glass Fiber Waste

Compound	Wt % of Total	Compound	Wt % of Total
Acetone	77	Styrene	0.2
Isopropyl Alcohol	08	1,2 Dichloroethane	0.2
Benzene	06	Naphthalene	0.2
Acrylonitrile	04	3-phenylfuran	0.1
Toluene	02	Xylene	0.1
2-Butanone	01	1-methyl naphthalene	0.1
1,1,1,2 tetrachloroethane	01	Others	0.1
Cyclopentanone	0.2	Total	100

These results suggest the following observations and comments:

1. About 97% of the emissions are acetone, isopropyl alcohol, benzene, acrylonitrile and toluene. These should be easily oxidizable at elevated temperatures in an after burner or by mixing this gas stream with the exhaust from the melting furnace before heat recovery.
2. The major VOCs among the evolved gases, acetone and isopropyl alcohol, can also be scrubbed by a water scrubber because they are soluble in water.
3. Several basic conceptual designs of the process were developed. Obviously, trade-off analysis of different integration concepts for particular applications will be necessary to select the most cost-effective design for each operation. Figure 8 illustrates an option for integrating the thermal treatment process with an existing glass fiber forming operation. Washed and shredded waste will be conveyed to the thermal-treatment reactor, which is in this concept the first of a two-chamber reactor system dedicated to processing waste glass only. In the first chamber the temperature is maintained slightly below the melting point of the glass. After the treatment is completed the conveyor moves the load out of the treatment chamber and into the high-temperature melting chamber. Molten glass is drawn from the melting chamber and is mixed with virgin molten glass and the mixture is sent through the bushings. Molten glass from glass waste can also be sent through dedicated bushings if mixing with virgin glass is not preferred or if the recovered

glass is to be used for a special application. A fraction of the combustion gases from the melting chamber is sent to the treatment chamber in order to maintain it at the desired temperature. Exhaust gases from the treatment chamber are first sent to a wet scrubber to remove any fugitive glass fibers and to scrub some of the VOCs that may have survived in the treatment chamber. The wet solids collected in the scrubber will be sent back to the treatment chamber and the water will be recycled into the scrubber. The scrubbed gas can be exhausted, or processed in an after burner if necessary.

4. Figures 4 and 8 and the experimental data we generated were used in consultation with industry on the potential value of the recovered glass fibers and were used to develop an approximate cost estimate for the process. The results are presented in Table 7.
5. The results reflect a potential payback of less than 2 years. As the cost of energy and disposal of this waste increases, so will the economic competitiveness of this process
6. Thermal treatment to remove the coating layer will also loosen up any metallic particulates that might be trapped in it, and the particulates could be removed by washing. Therefore, washing of the glass fibers could be done after thermal treatment instead of before it.

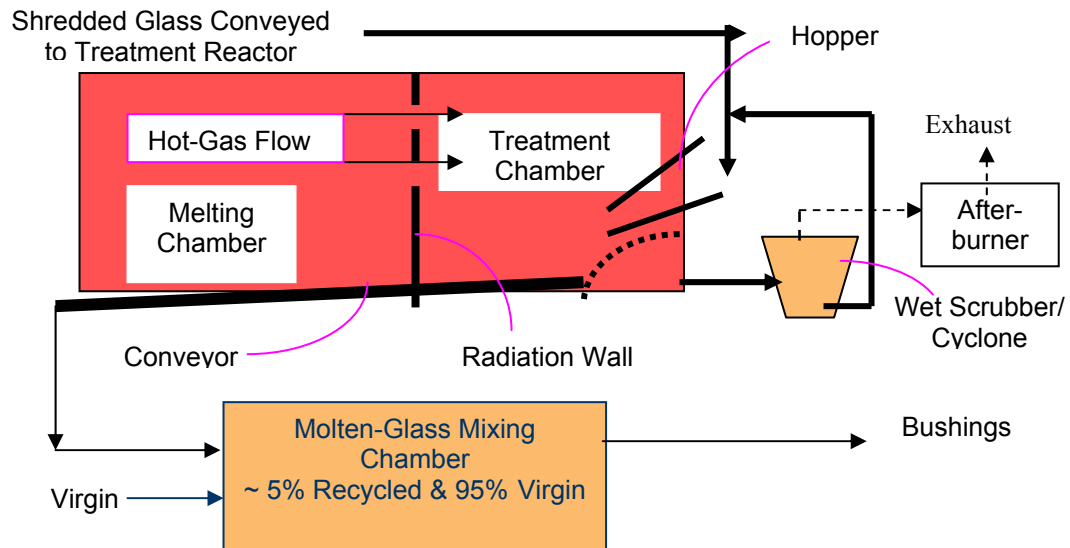


Figure 8. A Simplified Schematic Diagram of the Two-Chamber Waste-Glass Processing Reactor.

Table 7. Economic Analysis of the Thermal Treatment Process

<u>(Basis: 18,200 metric tons/yr of Glass-Fiber Waste)</u>		
REVENUES, \$1000/yr		
Recovered glass Fibers @ \$0.066/Kg	1,200	
TOTAL REVENUES		1,200
OPERATING COSTS, \$1000/yr		
Feedstock (credit for avoided disposal)	-500	
Waste disposal	0	
Utilities	160	
Labor	150	
Maintenance	50	
TOTAL OPERATING COSTS		-140
NET INCOME, \$1000/yr	1,340	
CAPITAL COST, \$1000	~2,000	

The research conducted on the thermal method leads to the following conclusions:

- (1) This method is technically feasible and economically attractive for removing contaminants off of glass fiber waste so that it could be recycled into value added products.
- (2) Heat and mass transfer considerations are important for complete removal of the polymeric-coating materials and of any by-products or their decomposition or oxidation.
- (3) Conducting the treatment at temperatures below the melting point of the glass is necessary in order to avoid the encapsulation of some of the coating material or its by-products in the molten glass.
- (4) Because the thermal treatment process can oxidize all kinds of polymeric-coating materials, including epoxies, it can process a mixture of waste glass materials containing different coatings. Therefore, pre-sorting of the waste is not necessary.
- (5) An adequate supply of air (oxygen) is necessary during the thermal treatment process to prevent thermal decomposition of some of the oxidation/pyrolysis products from the coating layer which could result in the deposition of finely-dispersed carbon particles on the fibers.
- (6) Washing the fibers before and/or after treatment reduces the metallic particulates of the fibers
- (7) Conveying of the glass-fiber waste before and after treatment should be done in a way to avoid the introduction of new contaminants into the glass stream. Even the best grades of steel abrade when contacted with glass in motion. Therefore, conveyor walls should be made of materials that do not introduce new contaminants. Silica-alumina conveyors may be used. Contact between conveyor walls and glass in motion should be kept to an absolute minimum in any case.

Chemical Treatment of the Coated Glass Fibers

We also tested and evaluated the chemical-treatment method for de-coating the glass-fiber waste. We also evaluated the resulting waste streams in order to identify appropriate environmental controls, and conducted economic evaluation of the process.

Hot tetraethylene glycol (TTEG) was successful in removing the coating layer off of the glass fiber surface. The required residence time was similar to that required by the thermal process. Typical results are presented in Table 8. The sample that was treated for 15 minutes (as shown in Table 8) was then washed in water and was essentially free of residual combustible material. However, the sample treated for 30 minutes had about 5 times as much combustible material. It may be that the second sample was not washed enough with water. This could have resulted in some glycol remaining on the sample. In general, the results demonstrate that this method is capable of removing the coating layer. Washing of the treated fibers is necessary to remove the chemicals of the surface. This process also produces wastewater.

In order to continue the evaluation of the chemical process we developed a conceptual design of the process, shown in Figure 9. The glass-fiber waste is first shredded to the appropriate size and then

chemically treated. Washing prior to treatment may or may not be necessary depending on whether the chemicals used are degraded by the coating material and on whether the excess coating solution is to be recovered or not. The treated fibers are then washed and recovered.

Table 8. Combustible Content of the Chemically-Treated Waste-Glass Samples

<u>Sample</u>	<u>Combustible Residual, PPM</u>
1. In TTEG* (300°C, 15 min)/ water wash	97
2. In TTEG (300°C, 30 min)/ water wash	492
*TTEG=Tetraethylene Glycol	

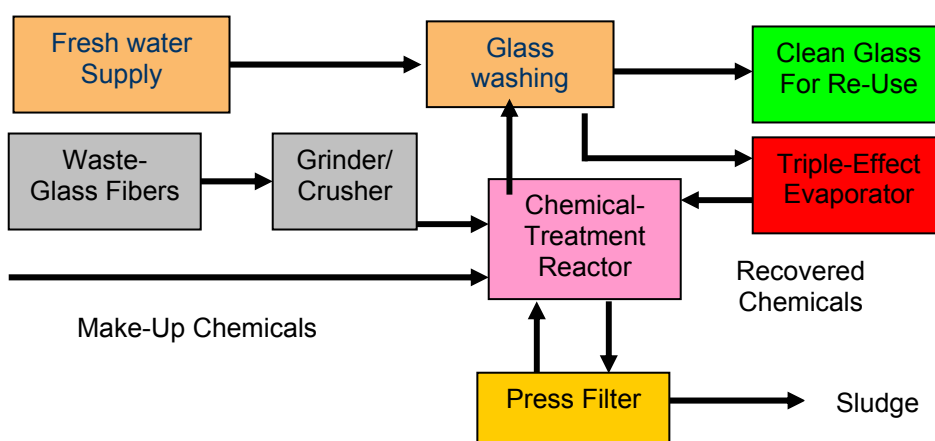


Figure 9. Conceptual Design for the Chemical Treatment Method.

We also estimated the amount of sludge (Table 9) and wastewater (Table 10) that this process will generate and used the information in performing an economic analysis of the process (Table 11).

Table 9. Sludge Production by the Chemical Method
Per Metric Ton of Glass-Fiber Waste Treated

Organic Coatings in the Sludge	3 KG
Glass Fibers in the Sludge	6 KG
Chemicals in Sludge	13.5 KG
Total Waste Generated	22.5 KG
Total Waste Generated	7 Gallons
<u>Estimated Disposal Cost</u>	<u>\$7/Metric Ton of Glass</u>

Table 10. Wastewater Produced by the Chemical Method
Per Metric Ton of Glass-Fiber Waste Treated

Wastewater	140 Gallons
Energy Cost for Evaporation of the Water & Recovery of the Chemicals @ \$5/Million Btu	\$5.80
Disposal Cost if Chemicals are Not Recovered	> \$100

The information given in Table 10 shows that evaporation of the water from the wastewater stream to recover the chemicals is less expensive than disposing of it. This conclusion is reflected in the conceptual design, Figure 9.

Table 11. Preliminary Economic Analysis of the Chemical Treatment Process

(Basis: Treatment of 18,200 metric tons of glass fiber waste per year)

REVENUES, \$1000/yr		
	Recovered glass Fibers @ \$0.066/KG 1,200	
TOTAL REVENUES		1,200
OPERATING COSTS, \$1000/yr		
	Feedstock (credit for avoided disposal)	-500
	Waste disposal	235
	Utilities & Chemicals	300
	Labor	150
	Maintenance	50
TOTAL OPERATING COSTS		235
NET INCOME, \$1000/yr		965
CAPITAL COST, \$1000		~2,000

The results show that this method has a potential payback of a little more than two years. It is longer than the payback of the thermal process. A comparison of the two methods is summarized in Table 12.

Table 12. Payback Comparison of the Thermal Treatment and Chemical Treatment Processes

Criterion	Thermal Process	Chemical Process
1. Potential Payback	< 2 years	> 2 years
2. Applicability to different coating materials	Applicable	Different chemicals may be required
3. Production of waste streams	Gaseous emissions (VOCs)	Liquid waste & VOCs
4. Adaptability to present glass production operations	Readily adaptable	A new technology

Based on the comparison shown in Table 12, we concluded that the thermal treatment process is the preferred process to develop and implement.

Fiberglass-Manufacturing Scrap

The fiberglass scrap on which we conducted the experiments was generated during the manufacturing of fiberglass panels like the one shown in Figure 10. The glass fibers here are held together with a polymeric-based binder.

Development of the Thermal Treatment Process for Fiberglass Scrap:

We conducted experiments on fiberglass scrap samples that were first shredded and then thermally treated in the presence of air. Treated and untreated fiberglass-scrap samples were then sent for chemical analysis to determine the degree of removal of the binder material. The thermal treatment process removed more than 99.5% of the combustible binder material in about 10 minutes as shown in Table 13 below. A picture of the thermally-treated fiberglass-scrap sample is shown in Figure 11. Fiberglass samples treated at temperatures above the melting point of the glass resulted in the entrapment of the polymeric-binder material as shown in Figure 12. Therefore, it is important to treat the fiberglass waste at temperatures below the melting point of its glass fibers.

The conceptual design for the fiberglass thermal treatment process is the same as the design for the glass-fiber waste material except that the fiberglass scrap does not require washing. The economic analysis of the fiberglass thermal treatment process is also essentially the same as the economic analysis for thermal treatment of the glass-fiber waste.

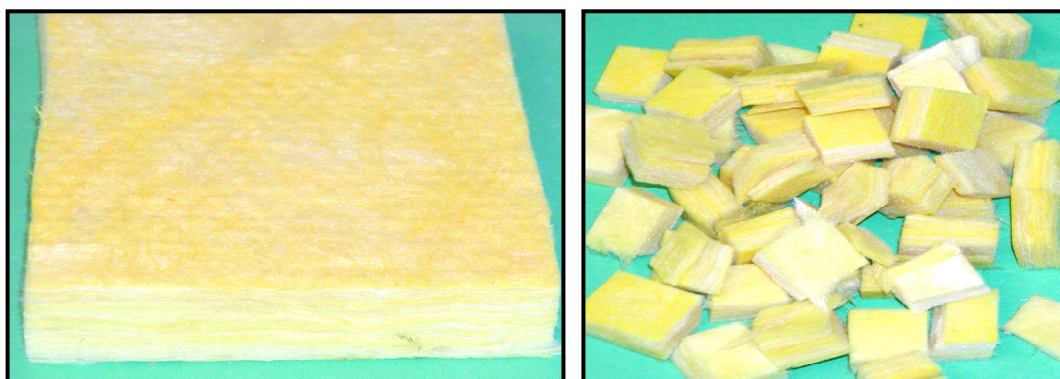


Figure 10. Fiberglass Scrap Sample “As Is” (Left) and After Shredding (Right).

Table 13. Combustible Materials on the Fiberglass-Scrap Panels
Before and After Thermal Treatment at 565°C

Sample Type	Treatment Time, Min	Residual Combustible PPM	% of Combustible Removed
1. Untreated Waste, Top Half*		108,978	0
2. Untreated Waste, Bottom Half*		154,101	0
3. Average for Untreated Waste		131,540	0
4. Thermally Treated Sample	10	426	99.7
5. Thermally Treated Sample	15	647	99.5
6. Thermally Treated Sample	20	642	99.5
7. Thermally Treated Sample	40	541	99.6
8. Thermally Treated Sample	45	536	99.6
9. Average for Treated Samples		558	99.6

* The binder material was not evenly distributed throughout the fiberglass panel.

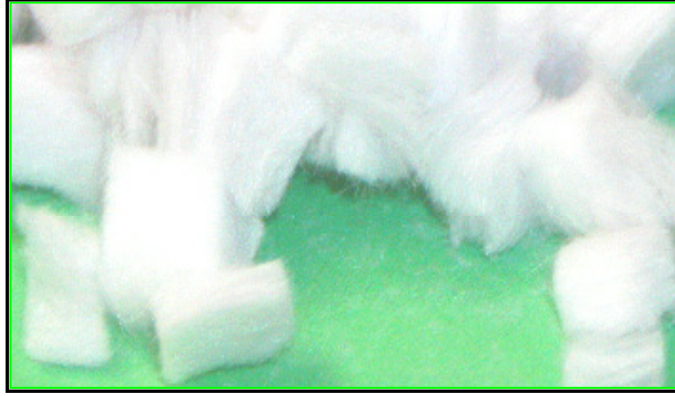


Figure 11. Thermally-Treated Fiberglass-Manufacturing Scrap.



Figure 12. Melting of the Fiberglass Scrap Resulted in the Entrapment of the Binder Material in the Molten Glass.

The gas collection system, shown in Figure 7, was also used to collect the gases that evolved during the thermal treatment of fiberglass scrap. The results are summarized in Table 14.

Table 14. Emitted Pollutants in an Oxygen Deficient Environment From Fiberglass Waste

Pollutant	% of total	Pollutant	% of total
Acetone	65	Diethyl ether	0.4
Acrylonitrile	21	Chloroethane	0.7
Vinyl Chloride	6	Chloromethane	0.6
Dimethyldifluorosilane	4		
Ethanol	3	Total	100

Our industrial partner, CertainTeed, successfully tested the process on fiberglass scrap in one of its plants. CertainTeed provided the simplified conceptual design used in testing the process, Figure 13. CertainTeed is “actively trying to put to use the information gained” from the research.

Waste Insulation Fiberglass Recycling Method

Steps

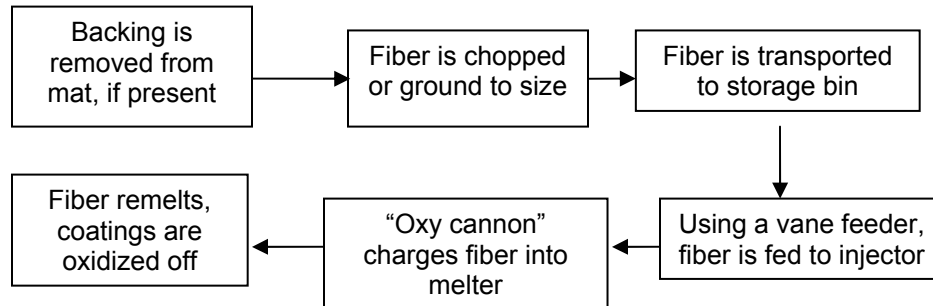


Figure 13. Simplified Schematic Diagram of the Waste Insulation Fiberglass Recycling Process at CertainTeed

Development of the Chemical Treatment Process for Fiberglass-Manufacturing Scrap

We conducted tests using different hot glycol/water, acid/water and base/water solutions to remove the polymeric-binder materials off of the fiberglass-scrap panels. In earlier tests done on fiberglass insulation batting material, the hot glycol/water solutions were effective in removing the polymeric-binder material. However, none of these solutions were effective in recovering the glass fibers from the fiberglass scrap panels that we obtained from CertainTeed in reasonable processing times. This proves that different chemicals will be required to treat different fiberglass scrap panels. This makes the chemical treatment process inferior to the thermal treatment process, which can treat different scrap that contains different polymeric binders in the same reactor.

Conclusions

The objective of this research project was to develop technology to enable the Glass Industry to recycle its glass-fiber waste. The research demonstrated the technical feasibility and cost effectiveness of recovering glass fibers suitable for recycling into value added products, from waste generated during the glass fiber manufacturing process and from fiberglass scrap. A process to recover the glass fibers was also developed and tested. The chemistry of the recovered glass fibers by this process from glass-fiber manufacturing waste was essentially the same as the chemistry of virgin glass. It removes essentially 100% of the polymeric coating layer off of the glass fiber manufacturing waste thereby reducing its total carbon content to less than 100 PPM, which is typical for virgin glass. It also removes most of the fine metallic particulates that abrade from the dies and during shredding, conveying and handling of the fibers during processing. The process is environmentally friendly and has a potential payback of less than 2 years. The process consists of two basic steps: (1) Washing of the waste fibers to remove excess coating solution and any tiny metal particles that abrade from the dies during the manufacturing process before they dry up on the fibers, and (2) Thermal treatment of the waste fibers at temperatures below the melting point of the fibers to breakdown and oxidize the polymeric coating layer on the waste fibers. The technology was tested in the laboratory in batch and in continuous reactors. Large scale testing of the process using fiberglass scrap was also conducted by CertainTeed in one of its plants.

According to the industry document Glass: A Clear Vision for a Bright Future "... use of recycled glass lowers energy costs alone, by an average of \$4 to \$9 per metric ton compared to solely using virgin raw

materials.” Therefore, this technology will help the glass fiber industry save money, keep this waste out of the landfill and save substantial amounts of energy.

Patents

Argonne National Laboratory filed two invention disclosures:

1. “Process to Recycle Glass Fiber Manufacturing Waste and Fiberglass Scrap.” Invention Disclosure Number ANL-IN-03-129. Inventors, Bassam Jody, Joseph Pomykala and Edward Daniels.
2. “A process to Produce Fiberglass Panels Having Black Surfaces.” Invention Disclosure Number ANL-IN-02-028. Inventors, Bassam Jody, Joseph Pomykala and Edward Daniels.

CertainTeed has also filed one invention disclosure. No further information is available on it at this time.

Publications/Presentations

B. J. Jody, J. A. Pomykala Jr., E. J. Daniels, J. C. Wells, and C. E. Davis, “A Process to Recycle Glass Fibers From Glass-Manufacturing Waste” presented at and published in the proceedings of the 2003 TMS Conference- EPD Congress, San Diego, Ca, March 3-6, 2003, pp 337-346.

Industrial Interest

A major glass fiber manufacturer contacted ANL and is “interested in pursuing a partnership that ultimately helps reduce waste to landfill ...and will commit resources to further this project along.”

Acknowledgment

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